Published in Encyclopedia of Physics, R. G. Lerner & G. L. Trigg (Eds.), Wiley-VCH (2005), 1866-1876

Organic Semiconductors

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Revision date: 24-02-2005

History

With the invention of the transistor around the middle of the last century, inorganic semiconductors such as Si or Ge began to take over the role as the dominant material in electronics from the previously dominant metals. At the same time, the replacement of vacuum tube based electronics by solid state devices initiated a development which by the end of the 20th century has lead to the omnipresence of semiconductor microelectronics in our everyday life. Now at the beginning of the 21st century we are facing a new electronics revolution that has become possible due to the development and understanding of a new class of materials, commonly known as *organic semiconductors*. The enormous progress in this field has been driven by the anticipation of novel applications, such as large area, flexible light sources and displays, low-cost printed integrated circuits or plastic solar cells from these materials.

Strictly speaking organic semiconductors are not new. The first studies of the dark and photoconductivity of anthracene crystals (a prototype organic semiconductor) date back to the early 20th century. Later, triggered by the discovery of electroluminescence in the 1960s, molecular crystals were intensely investigated by many researchers. These investigations established the basic processes involved in optical excitation and charge carrier transport (for reviews see, e. g., [1–3]). Nevertheless, in spite of the principal demonstration of organic electroluminescent diodes, there were several drawbacks preventing practical use of these early devices. For example, neither sufficient current and light output nor satisfying stability could be achieved. The main obstacles were the high operating voltage as a consequence of the crystal thickness (in the micrometer to millimeter range) together with the difficulties in scaling up crystal growth as well as preparing stable, injection-efficient contacts to them.

Since the 1970s, the successful synthesis and controlled doping of conjugated polymers established the second important class of organic semiconductors, which was honored with the Nobel Prize in Chemistry in the year 2000 [4]. Together with organic photoconductors these conducting polymers have initiated the first applications of organic materials as conductive coatings [5] or photoreceptors in electrophotography [6].

The interest in undoped organic semiconductors revived in the 1980s due to the demonstration of an efficient photovoltaic cell incorporating an organic hetero-junction of p- and n-conducting materials [7] as well as the first successful fabrication of thin film transistors from conjugated polymers and oligomers [8–10]. The main impetus, however, came from the demonstration of high-performance electroluminescent diodes from vacuum-evaporated molecular films [11] and from conjugated polymers [12]. Owing to the large efforts of both academic and industrial research laboratories during the last 15 years, organic light-emitting devices (OLEDs) have progressed rapidly and meanwhile lead to first commercial products incorporating OLED displays. Other applications of organic semiconductors, e. g., as logic circuits with organic field-effect transistors (OFETs) or organic photovoltaic cells (OPVCs) are expected to follow in the near future.

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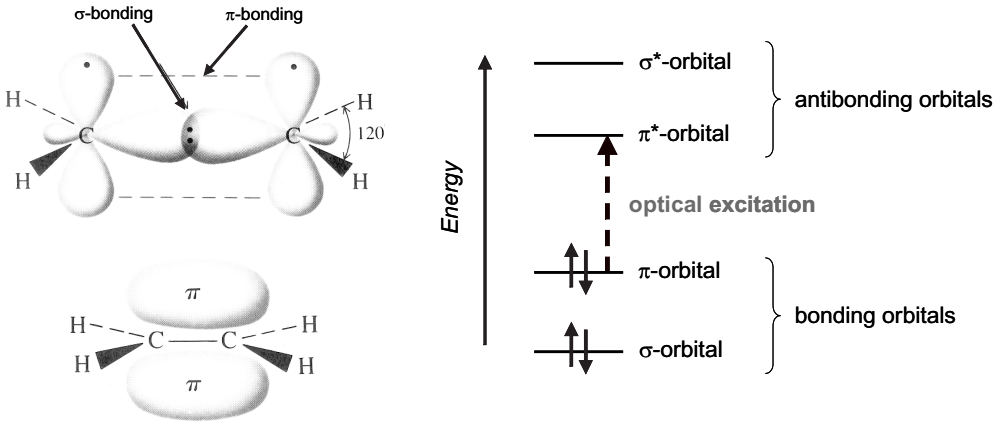

Fig. 1: Left: σ and π bonds in ethane, as an example for the simplest conjugated π electron system. The right graph shows the energy levels of a π-conjugated molecule. The lowest electronic excitation is between the bonding π orbital and the antibonding π^* orbital.

Materials

There are two major classes of organic semiconductors: low-molecular weight materials and polymers (for an overview see, e. g., [13]). Both have in common a conjugated p-electron system formed by the p_z orbitals of sp^2-hybridized C atoms in the molecules (see Fig. 1). In comparison to the σ bonds constituting the backbone of the molecules, π bonding is significantly weaker. Therefore, the lowest electronic excitations of conjugated molecules are the π–π^* transitions with an energy gap typically between 1.5 and 3 eV leading to light absorption or emission in the visible spectral range. In detail, the electronic properties of a molecule depend on factors like the conjugation length or the presence of electron donating or withdrawing groups. Thus organic chemistry offers a wide range of possibilities to tune the optoelectronic properties of organic semiconducting materials. Some prototype materials are given in Fig. 2.

An important difference between the two classes of materials lies in the way how they are processed to form thin films. Whereas small molecules are usually deposited from the gas phase by sublimation or evaporation, conjugated polymers can only be processed from solution, e. g., by spin-coating or printing techniques. Additionally, a number of low-molecular weight materials can be grown as single crystals allowing intrinsic electronic properties to be studied on such model systems. The controlled growth of highly ordered thin films either by vacuum deposition or solution processing is still a subject of ongoing research, but will be crucial for many applications (see, e. g., [14]).

Basic Properties of Organic Semiconductors

The nature of bonding in organic semiconductors is fundamentally different from their inorganic counterparts. Organic molecular crystals are van-der-Waals-bonded solids implying a considerably weaker intermolecular bonding as compared to covalently bonded semiconductors like Si or GaAs. The consequences are seen in mechanical and thermodynamic properties such as reduced hardness or lower melting point, but even more importantly in a much weaker

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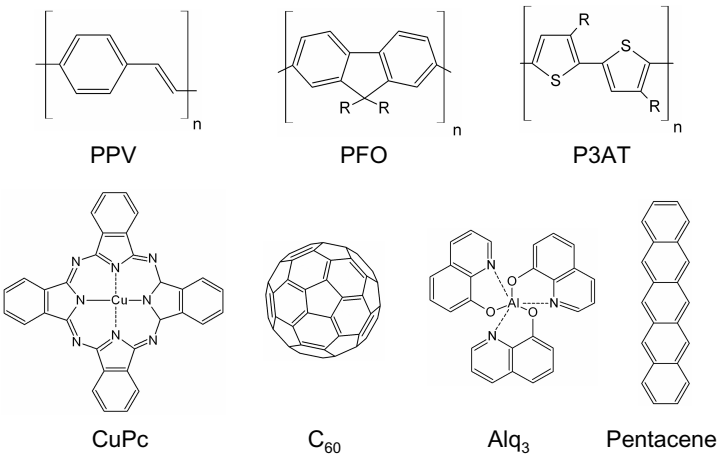

Fig. 2: Molecular structure of some prototype organic semiconductors: PPV, poly(*p*-phenylenevinylene); PFO, polyfluorene; P3AT, poly(3-alkylthiophene); Alq_3, tris(8-hydroxyquinoline)aluminium; fullerene, C_{60}; CuPc, Cu-phthalocyanine; pentacene.

delocalization of electronic wavefunctions amongst neighboring molecules, which has direct implications for optical properties and charge carrier transport. The situation in polymers is somewhat different since the morphology of polymer chains can lead to improved mechanical properties. Nevertheless, the electronic interaction between adjacent chains is usually also quite weak in this class of materials.

Optical Properties

Owing to the weak electronic delocalization, as a first-order approximation the optical absorption and luminescence spectra of organic molecular solids are very similar to the spectra in the gas phase or in solution (apart from a solvent shift). In particular, intramolecular vibrations play an important role in solid state spectra and often these vibronic modes can be resolved even at room temperature. Thus the term "oriented gas" is sometimes used for molecular crystals. Nevertheless, solid state spectra can differ in detail with respect to selection rules, oscillator strength and energetic position; moreover, due to the crystal structure or the packing of polymer chains a pronounced anisotropy can be found. Additionally, disordered organic solids usually show a considerable spectral broadening.

As a consequence of this weak electronic delocalization, organic semiconductors have two important peculiarities as compared to their inorganic counterparts. One is the existence of well-defined spin states (singlet and triplet) as in isolated molecules which has important consequences for the photophysics of these materials (see Fig. 3). Usually the ground state of an organic molecule is a singlet state (S_0) and absorption of a photon leads to the first excited singlet state (S_1). Thereby the Franck–Condon factor determines the relative intensities of the vibronic transitions within this manifold. Typical lifetimes of the S_1 state are in the range 1–10 ns, thus leading to a rapid transition back to the S_0 ground state via fluorescence or nonradiative transitions. In the excited singlet state there is a small probability for intersystem crossing to the triplet state (T_1), from which the excitation energy can be released either by

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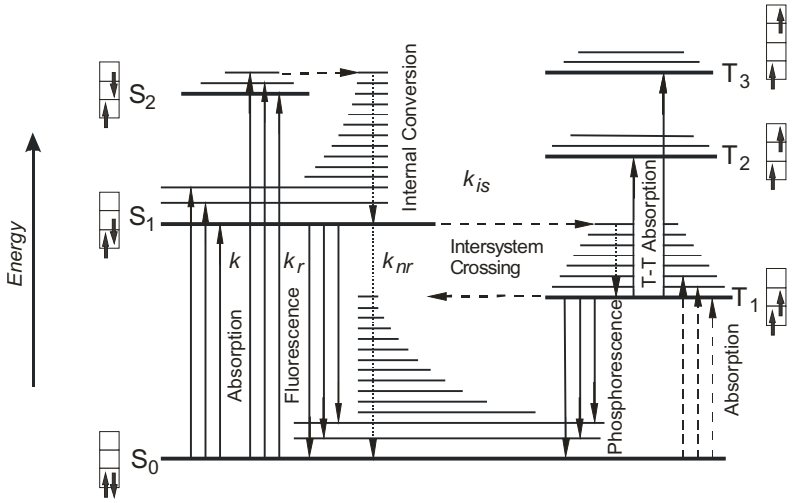

Fig. 3: Energy level scheme of an organic molecule (left: singlet manifold, right: triplet manifold). Arrows with solid lines indicate radiative transitions, those with broken lines nonradiative transitions.

phosphorescence or non-radiatively. However, since intersystem crossing is a weak process, triplet lifetimes are usually in the millisecond range for pure aromatic hydrocarbons, and radiative decay via phosphorescence is usually not observed at room temperature. This also sets an upper limit for the electroluminescence quantum efficiency in OLEDs as about 75% of the excited states formed by the recombination of injected electrons and holes are in the triplet state. Triplet lifetimes can be considerably shorter in molecules incorporating heavy atoms, such as Pt or Ir. Therefore metal organic complexes incorporating these elements are becoming more and more important in OLEDs. A second important difference originates from the fact that optical excitations ("excitons") are usually localized on one molecule and therefore have a considerable binding energy. A simple estimation as the Coulomb energy of an electron-hole pair localized at a distance of 10 Å in a medium with a dielectric constant of 3 yields a value of about 0.5 eV for the exciton binding energy. In photovoltaic cells this binding energy has to be overcome before a pair of independent positive and negative charge carriers is generated.

Charge Carrier Transport

When transport of electrons or holes in an organic molecular solid is considered, one has to bear in mind that this involves ionic molecular states. In order to create a hole, e. g., an electron has to be removed to form a radical cation M^+ out of a neutral molecule M. This defect electron can then move from one molecule to the next. In the same way, electron transport involves negatively charged radical ions $M^{\cdot -}$ (qualitatively, the same arguments hold for polymers, however, in this case charged states are usually termed positive or negative polarons.) As compared to isolated molecules in the gas phase, these ionic states are stabilized in the solid by polarization energies leading to an energy level scheme as shown in Fig. 4. From this diagram one can clearly see that due to the already mentioned exciton binding energy the

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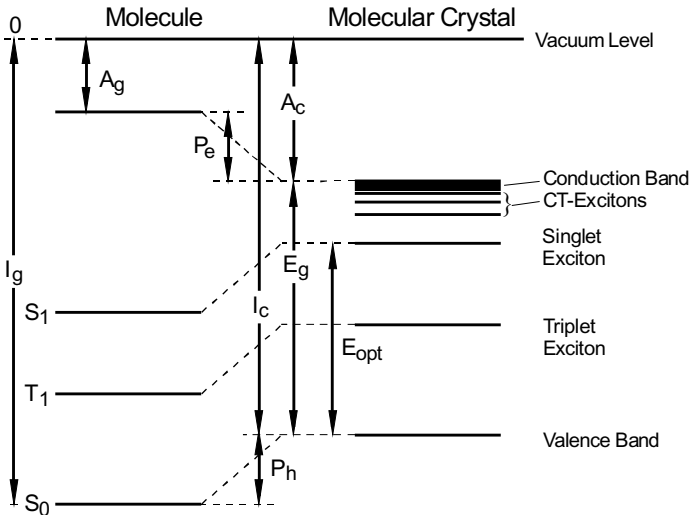

Fig. 4: Energy levels of an isolated molecule (left) and a molecular crystal (right): I_g and A_g denote the ionization potential and electron affinity in the gas phase, I_c and A_c the respective quantities in the crystal. Due to the polarization energies P_h and P_e charged states are stabilized in the crystal. E_g is the single-particle gap being relevant for charge carrier generation, whereas E_{opt} denotes the optical gap measured in absorption and luminescence. Their difference is the so-called exciton binding energy.

optical gap between the ground state and the first excited singlet state is considerably smaller than the single particle gap to create an uncorrelated electron–hole pair. In going from molecular crystals to disordered organic solids one also has to consider locally varying polarization energies, due to different molecular environments, which lead to a Gaussian density of states for the distribution of transport sites as shown in Fig. 5.

Thus, depending on the degree of order, the charge carrier transport mechanism in organic semiconductors can fall between two extreme cases: band or hopping transport. Band transport is typically observed in highly purified molecular crystals at low temperatures. However, since electronic delocalization is weak the bandwidth is small in comparison to inorganic semiconductors (typically a few kT at room temperature). Therefore room temperature mobilities in molecular crystals reach only values in the range 1 to $10\,\mathrm{cm}^2/\mathrm{Vs}$. As a characteristic feature of band transport the temperature dependence follows a power law behaviour

$$\mu \propto T^{-n} \quad \text{with} \quad n = 1 \ldots 3 \tag{1}$$

upon going to lower temperature. However, in the presence of traps significant deviations from such a behavior are observed.

In the other extreme case of an amorphous organic solid hopping transport prevails which leads to much lower mobility values (at best around $10^{-3}\,\mathrm{cm}^2/\mathrm{Vs}$, in many cases however much less). Instead of a power law the temperature dependence then shows an activated behavior with activation energies ΔE between 0.4 and 0.5 eV and the mobility also depends

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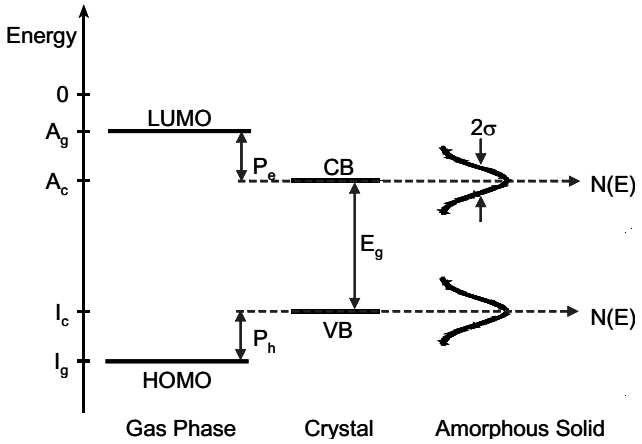

Fig. 5: Energy levels of an isolated molecule (left), a molecular crystal (middle) and an amorphous solid (right).

on the applied electric field [6]:

$$\mu(F,T) \propto \exp\left(-\frac{\Delta E}{kT}\right) \exp\left(\frac{\beta\sqrt{F}}{kT}\right) . \tag{2}$$

Alternatively, the mobility can also be described by the expression [6, 15]

$$\mu(F,T) \propto \exp\left(-\left[\frac{2\sigma}{3kT}\right]^2\right) \exp\left\{C\left(\left[\frac{\sigma}{kT}\right]^2 - \Sigma^2\right)\sqrt{F}\right\} , \tag{3}$$

where the disorder parameter σ (the width of the Gaussian density of states) is typically in the range of 80–120 meV.

Organic Semiconductor Devices

On a macroscopic level, the current through a material is given by the charge carrier density n and the carrier drift velocity v, where the latter can be expressed by the mobility μ and the electric field F:

$$j = env = en\mu F . \tag{4}$$

One has to bear in mind that in contrast to metals there is usually not a linear relation between j and F since both the carrier density and mobility can depend on the applied field. According to this equation, apart from the field, the two parameters n and μ determine the magnitude of the current. Thus it is instructive to compare their typical values with inorganic semiconductors and discuss different ways to control them.

As already mentioned above, the mobility strongly depends on the degree of order and purity in organic semiconductors and therefore to a great extent on the preparation and growth conditions. It can reach values of 1–10 $\mathrm{cm}^2/\mathrm{Vs}$ in molecular crystals, but values as low as $10^{-5}\,\mathrm{cm}^2/\mathrm{Vs}$ in amorphous materials are also not unusual. The highest mobility values

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achievable in thin films are nowadays comparable to amorphous silicon which is of course orders of magnitude less than crystalline Si.

The second parameter is the charge carrier density n. The intrinsic carrier density in a semiconductor with an energy gap E_g and an effective density of states N_0 (which is equal to the density of molecules in an organic semiconductor) is given by:

$$n_i = N_0 \exp\left(-\frac{E_g}{2kT}\right) . \tag{5}$$

Taking typical values of $E_g = 2.5\,\mathrm{eV}$ and $N_0 = 10^{21}\,\mathrm{cm}^{-3}$ leads to a hypothetical carrier density of $n_i = 1\,\mathrm{cm}^{-3}$ at room temperature, which is of course unattainable since impurities will lead to much higher densities in real materials. Nevertheless, the corresponding value for Si ($E_g = 1.12\,\mathrm{eV}$ and $N_0 = 10^{19}\,\mathrm{cm}^{-3}$) is with $n_i = 10^{10}\,\mathrm{cm}^{-3}$ many orders of magnitude higher, which demonstrates that organic semiconductors have extremely low conductivity if they are pure enough. In order to overcome the limitations posed by the low intrinsic carrier density, different means to increase the carrier density in organic semiconductors can be applied. These are:

(i) (electro-)chemical doping,

(ii) carrier injection from contacts,

(iii) photogeneration of carriers, and

(iv) field-effect doping.

In the following section these methods will be briefly discussed together with their application in various device structures.

Device Architectures and Properties

(i) Controlled doping has been one of the keys for the success of semiconductor microelectronics. There have been efforts to use tools like ion implantation doping for organic semiconductors as well; however, due to the concomitant ion beam damages and the need for sophisticated equipment, this method is probably not suitable for organic devices. Other techniques of doping have been successfully applied. These are chemical doping by adding strong electron donors or acceptors or electrochemical doping [16, 17]. At this point one should also mention that unintentional doping of organic materials often occurs during the synthesis or handling of the materials since in many cases ambient oxygen causes p-type doping of organic materials. Thus at present, controlled doping in organic semiconductors is still in its infancy and needs further investigation before it can be employed as a powerful tool for organic electronics.

(ii) Injection of charge carriers from contacts is the process that essentially governs device operation in organic light-emitting devices (OLEDs) (see Fig. 6a). This requires low energetic barriers at the metal-organic interfaces for both contacts to inject equally large quantities of electrons and holes, which is necessary for a balanced charge carrier flow. Thus the interface energetic structure plays a very crucial role for achieving efficient OLEDs [18]. Another process that comes into play is space-charge limitation of the

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current. Due to relatively high electric fields being applied to OLEDs (typically 5 to 10 V across a layer thickness of 100 nm yield $F = 0.5$–$1\,\mathrm{MV/cm}$), materials with low mobility still yield sufficiently large current densities for display applications. This is a consequence of the space-charge limited current scaling with the third power of the reciprocal thickness [19]:

$$j_{\mathrm{SCLC}} = \frac{9}{8}\varepsilon\varepsilon_0\mu\frac{V^2}{d^3}\ . \tag{6}$$

Apart from charge carrier transport, the efficiency of OLEDs is also strongly influenced by photophysical processes. First of all, materials with a high fluorescence quantum yield are required. However, since a large fraction of the excited states formed by charge carrier recombination are triplets, the most efficient OLEDs nowadays make use of energy transfer to so-called triplet emitters, where the presence of heavy metals allow the transition from the triplet state to the ground state via phosphorescence [20].

(iii) Another important device application of organic semiconductors is in organic photovoltaic cells (OPVCs) (see Fig. 6b). In spite of their high absorption coefficient, which exceeds $10^5\,\mathrm{cm}^{-1}$ in most materials, the application of organic semiconductors in OPVCs faces the problem of the large exciton binding energy which prohibits efficient exciton dissociation. This can be overcome by making use of a photoinduced charge transfer between an electron donor like PPV and the fullerene C_{60} as an acceptor [21]. Due to the short exciton diffusion length of typically 10 nm, efficient OPVCs use the so-called bulk-heterojunction concept of mixing donor and acceptor in one single layer. In spite of the huge progress recently achieved, there are still challenges to achieve sufficient lifetime of OPVCs under ambient conditions or the availability of low-band gap materials to make better use of the solar spectrum [22].

(iv) Organic field-effect transistors (OFETs) (see Fig. 6c) are 3-terminal devices in which the charge carrier density in the channel between source and drain contacts can be controlled by the applied gate voltage across a thin dielectric [23, 24]. The drain current is then given by

$$I_{\mathrm{D}} = \frac{W}{L}C_i\mu(V_{\mathrm{G}} - V_{\mathrm{T}})V_{\mathrm{D}} \tag{7}$$

in the linear region, and by

$$I_{\mathrm{D}} = \frac{W}{2L}C_i\mu(V_{\mathrm{G}} - V_{\mathrm{T}})^2 \tag{8}$$

in the saturation regime. Here W/L denotes the ratio between channel width and length, C_i the specific insulator capacitance and V_{T} the threshold voltage. Thus the performance of OFETs can be tuned to some degree by using suitable geometries with short channel length L or thin insulating layers of materials with high dielectric constant, but it is clear that the mobility μ also needs to be high (in the range of amorphous Si) to enable switching at frequencies significantly higher than 100 kHz which will be needed for more demanding applications in the future. This requires materials and methods to grow highly ordered organic semiconductor films. A further challenge will be to realize CMOS-like organic integrated circuits by using materials with stable *p*- and *n*-conducting properties.

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Summary and Outlook

About 50 years after the invention of Si-based transistors, which nowadays are the basis of modern electronic devices, recent years have seen the development of organic semiconductors as a new class of active materials for electronic and optoelectronic applications. The joint effort in materials development, fundamental research and device engineering (for reviews see, e. g., [25, 26]) have meanwhile lead to the first commercial products using organic semiconducting materials in flat panel displays. Other applications of organic semiconductors, e.g. as active components in flexible electronics or light-harvesting devices are expected to follow in the near future.

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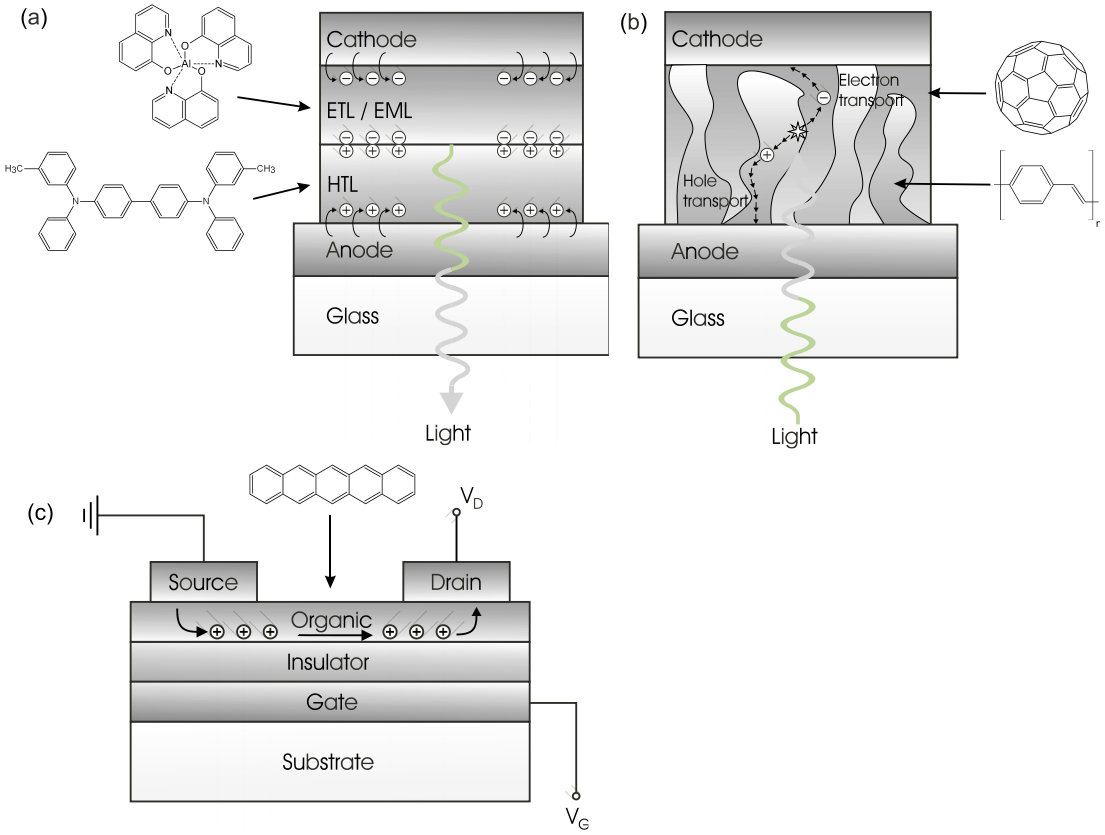

Fig. 6: Different types of organic semiconductor devices. (a) Organic light-emitting diode (OLED): Typically, a heterolayer structure is used, where HTL stands for hole transport layer and ETL for electron transport layer, EML denotes the emission layer. Instead of the displayed combination of a triphenylamine derivative and Alq_3, polymeric OLEDs usually employ a conductive polymer (PEDOT:PSS) together with luminescent polymers like PPV or PFO derivatives. (b) Organic photovoltaic cell (OPVC): The so-called bulk-heterojunction devices usually consist of a mixture of soluble PPV (or P3AT) and fullerene derivatives. Alternatively, mixed layers of evaporated small molecules like CuPc and C_{60} can be used. (c) Organic field-effect transistor (OFET): Prototypical materials in *p*-channel OFETs are pentacene as a low molecular weight material and P3AT as a conjugated polymer, respectively. Among others, C_{60} can be employed in *n*-channel transistors.